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PROPERTIES OF THIN-FILM GLASS COATINGS PRODUCED BY LASER DEPOSITION IN VACUUM

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The paper considers processes occurring in heat treatment and corrosive-medium action on thin films of lead-borate glasses with additives of CoO , ZrO_2 , Sb_2O_5 , V_2O_5 , MoO_3 , deposited in vacuum with pulse treatment of the initial material using a neodymium laser. It is shown that use of this method makes it possible to form films with a vitreous phase that is more resistant to annealing and corrosion than similar films obtained by thermal evaporation in vacuum.

Thin (up to 1 μm) inorganic vitreous oxide films occupy an important place among passive thin-film coatings and active thin-film elements in solid-body electronics, integral optics, etc. The methods for production of thin films (sedimentation, electrostatic deposition, sol-gel technology, precipitation from the vapor phase, vacuum deposition) make it possible in some cases to attain a ratio of the components that would be impossible using traditional methods. Moreover, each of these methods, especially ones where the initial material is subjected to a high-energy effect, has a specific influence on the physicochemical properties of the resulting films. Therefore, a correlation between the properties of solid glasses and films based on these glasses is not always possible. Obviously, the scale effect by itself has a strong influence on the change in the glass properties in passage to a quasi-two-dimensional state.

Research carried out in this field in recent years mostly dealt with the development of methods for producing thin glass films and studying their physical (mechanical, optical, electrical, etc.) properties. [1–4]. A small number of papers were devoted to the stability of thin glass films under the effect of a corrosive medium and temperature, which are the most important technological factors in the manufacture of products and instruments using thin films [5–7].

The authors earlier carried out research on the processes induced by temperature and corrosive-medium action in glass films based on lead-borate and lead-boron-silicate glasses and revealed the main features of these processes in films obtained by thermal evaporation in vacuum [8, 9]. It was found that the properties of thin glass films are virtually

impossible to predict based on the properties of the initial glasses. Therefore, it was of interest to use a more high-energy method of vacuum formation of thin glasses films the initial material. One of these methods is pulsed laser deposition in vacuum, which is successfully implemented to produce thin films on the basis of individual inorganic oxides or compositions of them [10, 11].

The present paper considers the effect of post-deposition annealing and an aqueous corrosive medium with neutral and acid reactions on lead-borate thin glass films, as compared to the effect of the same factors on the initial solid glasses. The purpose of the paper is to elucidate the effect of the initial-material composition on the heat and corrosion resistance of thin-film coatings deposited by laser radiation emitted from initial targets to single-crystal silicon substrates. The selection of the lead-borate system results from its wide application as a substrate in protective and passive coatings in microelectronics [12].

The initial materials were lead-borate glasses of the compositions $0.45 \text{ PbO} - 0.45 \text{ B}_2\text{O}_3 - 0.1 \text{ M}_n\text{O}_m$ and $0.4 \text{ PbO} - 0.4 \text{ B}_2\text{O}_3 - 0.2 \text{ M}_n\text{O}_m$. The doping additives M_nO_m introduced into the glasses were V_2O_5 , Sb_2O_5 , CoO , ZrO_2 , and MoO_3 (their content was 10 and 20%; here and elsewhere molar content is indicated). Mixtures consisting of the corresponding components (chemically pure PbO , H_3BO_3 , and metal oxides, carbonates, or nitrates) were melted in corundized crucibles in a silite furnace at a temperature of $1100 - 1250^\circ\text{C}$ for 20 min with subsequent casting on a metal plate.

The physicochemical properties of the glasses obtained in this way were determined by the standard methods: the thermal coefficient of linear expansion (TCLE) within the temperature interval of $20 - 400^\circ\text{C}$ and the softening start

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point (SSP) of samples 50 ± 2 mm high and 4 ± 1 mm in diameter annealed at a temperature of 400°C were determined on a DKV-5A dilatometer at a heating rate of $2^\circ\text{C}/\text{min}$, and the water and acid resistance was determined by the powder method based on the relative mass loss of powder with a particle size of $0.25 - 0.50$ mm. IR transmission spectra of glass powders pressed in KBr tablets were recorded on a Perkin-Elmer 457 spectrophotometer. X-ray patterns of samples were obtained on a DRON-3 instrument, and the glass-film thickness was measured by an MII-4 microinterferometer.

Disk-shaped glasses 20 mm in diameter were used as targets for vacuum formation of glass coatings. The pulsed-radiation source was a neodymium laser in the free-generation mode with a radiating wavelength of $1.06 \mu\text{m}$, a pulse duration of 1 msec, a target spot diameter of 2 mm, and a pulse energy of 150 J. The oxygen pressure in the space under the cap was maintained within the limits of $5.33 - 10.66 \text{ Pa}$ ($4 \times 10^{-2} - 8 \times 10^{-2} \text{ mm Hg}$). Substrates that were washed in peroxyammonium and peroxyformic acid solutions before inserting them into the laser device were heated by an IR lamp to temperature of 160°C in the course of film deposition. The rate of film deposition was $0.03 - 0.06 \mu\text{m}$ per pulse.

The thermal properties of the films obtained are presented in Table 1. It can be seen that the dopants in general produce an increase in the SSP of the tested glasses and hence an understandable decrease in their TCLE, as compared to the lead-borate glasses (except for V_2O_5), although an increase in the concentration of different additives can have a nonmonotonic effect on the variation of the thermal properties of the glass.

Immediately after production, glasses containing vanadium, antimony, molybdenum, and zirconium oxides were

TABLE 1

Doping additive	SSP, $^\circ\text{C}$	TCLE, $10^{-7} \text{ }^\circ\text{C}^{-1}$
No additive	417	97
V_2O_5 :		
10%	475	99
20%	450	131
MoO_3 :		
10%	466	95
20%	520	95
Sb_2O_5 :		
10%	450	76
20%	480	71
ZrO_2 :		
10%	485	74
20%	445	78
CoO :		
10%	434	67
20%	420	73

already crystallized to a certain extent. According to x-ray phase analysis data, the main crystal phases are formed by the following compounds (the principal recorded values of interplanar distances are indicated below, with ASTM data following in brackets): PbSb_2O_6 — 3.49 (3.49), 2.70 (2.69), 2.66 (2.65), 1.892 (1.887), 1.671 (1.670); ZrO_2 — 3.17 (3.16), 2.85 (2.83); $\text{Pb}_4\text{V}_2\text{O}_9$ — 3.14 (3.17), 2.97 (3.02), 2.13 (2.12), 2.03 (2.04), 1.94 (1.95); PbMoO_4 — 3.22 (3.22), 2.72 (2.71), 2.02 (2.02), 1.79 (1.79), 1.65 (1.65).

The corrosion resistance of the glasses immediately after production and after heat treatment (in the latter case, in the form of a finely disperse powder at a temperature of 320°C for 24 h) were measured with respect to water and an HNO_3 solution ($\text{pH} = 4$) at room temperature (Table 2).

It can be seen that introduction of 10% additive does not significantly alter the corrosion resistance, and with 20% additive the most evident changes are observed in vanadium- and cobalt-containing glasses. Whereas introduction of V_2O_5 brings about a substantial decrease in the glass resistance to both media, with use of CoO , on the other hand, an increase in its content produces marked improvement in the corrosion resistance to both media.

When the heat treatment or the corrosive-medium action bring about significant alterations of the composition and structure of the glasses, these changes are clearly reflected in their IR spectra (Fig. 1). The spectra of easily crystallized glasses typically exhibit a significant increase in the intensity of the narrow absorption band in the region of

TABLE 2

Doping additive	Corrosion resistance of glass, %*			
	without heat treatment		heat-treated	
	H_2O	HNO_3	H_2O	HNO_3
No additive	0.84	1.19	0.81	1.71
V_2O_5 :				
10%	1.04	1.30	0.98	2.70
20%	7.15	9.70	5.22	6.62
MoO_3 :				
10%	1.25	1.20	0.87	2.41
20%	0.60	1.84	0.49	2.37
Sb_2O_5 :				
10%	1.08	1.83	1.32	3.13
20%	1.58	3.66	3.00	3.38
ZrO_2 :				
10%	0.62	1.11	1.23	3.14
20%	0.79	2.00	0.73	2.41
CoO :				
10%	0.88	1.63	0.91	2.11
20%	0.37	1.08	0.25	1.05

* Mass losses after 6 days of the corrosive-medium effect at room temperature.

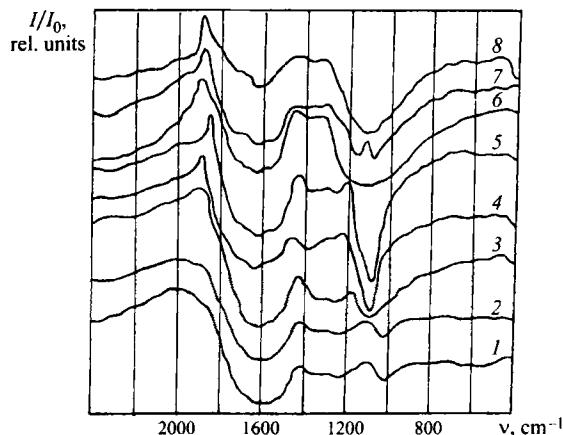


Fig. 1. IR spectra of solid glass (annealing duration 24 h, temperature 320°C): non-doped: 1) immediately after manufacture; 2) after annealing, doped with MoO_3 : 3) 10%, after manufacture; 4) 20%, after manufacture; 5) 20%, after annealing; doped with V_2O_6 : 6) 20%, after manufacture; 7) 20%, after annealing; 8) 20% after the effect of a corrosive medium at pH = 7 for 6 days.

700 – 800 cm^{-1} (Fig. 1, curves 3 – 5) or the appearance of a number of such bands in the same region, which is caused by an increased content of the crystalline phase. The effect of a corrosive medium on the least resistant glasses is also reflected in the IR spectra (Fig. 1, curve 8): the intensity of the absorption band in the range of 1500 – 1150 cm^{-1} caused by vibrations of B – O bonds in structural fragments containing three-coordination boron [13] weakened markedly due to washing out of these fragments.

The principal changes in the IR spectra of the considered glass films under heat treatment and corrosion are shown in Table 2.

All the films have wide absorption bands in the region of 2000 – 4000 cm^{-1} , which is typical of IR spectra of borate glasses. The longwave band (1150 – 800 cm^{-1}) related to B – O bond vibrations in structural fragments with four-coordination boron, similar to the IR spectra of solid glasses, usually exhibits lower intensity compared to the shortwave band (see Fig. 2, curve 1). In the course of annealing in air at a temperature of 320°C, a typical change in the film spectra is redistribution of the intensities of these bands, which points to rearrangement of the glass-forming skeleton caused by transition of part of the boron from three-coordination to four-coordination (Fig. 2, curve 2). This process requires the presence of oxygen. In annealing in vacuum, the IR spectra do not change.

Another process that can be induced in films by heat treatment is phase separation when the crystal phase is released. Phase separation in films is also manifested in the appearance of one or several narrower absorption bands in the IR spectra in the region of 800 – 600 cm^{-1} (see Fig. 2, curves 3 and 4). A special feature of phase separation in glass films formed by thermal evaporation in vacuum consists in its stochastic nature, and with a certain degree of

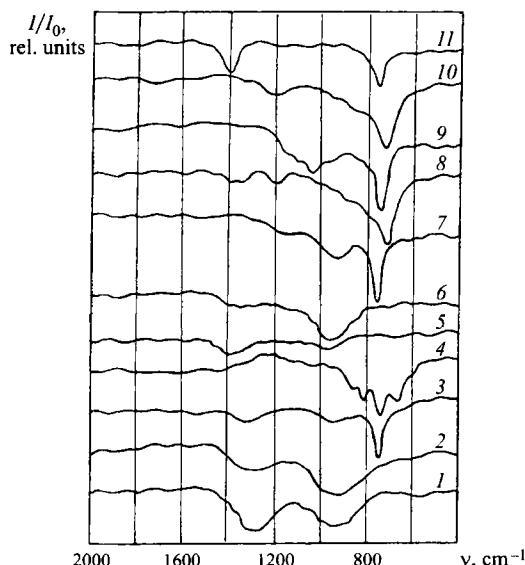


Fig. 2. IR spectra of thin glass films (annealing duration 24 h, temperature 320°C, duration of corrosive-medium effect: 6 h at pH = 6 and 1 h at pH = 4): 1) non-doped, immediately after deposition; 2) non-doped, after annealing; 3) 20% MoO_3 , after annealing; 4) 20% V_2O_5 , after annealing; 5) non-doped, not annealed after the corrosive-medium effect at pH = 7; 6) non-doped, annealed after the corrosive-medium effect at pH = 7; 7) 10% MoO_3 , annealed after the corrosive-medium effect at pH = 7.8; 8) 10% V_2O_5 , annealed after the corrosive-medium effect at pH = 7; 9) 10% MoO_3 , annealed after the corrosive-medium effect at pH = 4; 10) 10% V_2O_5 , annealed after the corrosive-medium effect at pH = 4; 11) 20% MoO_3 , after the corrosive-medium effect at pH = 7.

probability the crystalline phase can appear in any film, regardless of its composition [14]. As a result, both processes, namely, the rearrangement and the phase separation can compete kinetically. In the case of laser-deposited films no competition between these processes was observed, and phase separation occurred only in glasses whose compositions (containing molybdenum and vanadium) are the most prone to crystallization or in solid glasses, whereas in the rest of the films only structural rearrangement took place. This is apparently due to the fact that with laser evaporation, the effect of high-energy plasma on the growing film results in formation of films with a denser structure that, accordingly, includes a vitreous phase that is more stable to thermal action.

The rates of the indicated processes differ significantly. Whereas phase separation ends after 1.5 – 2 h of annealing, compaction of the film structure requires up to 24 h of annealing. Compaction occurs to the fullest extent in films that are not doped with additives. Non-heat-treated films are subjected to uniform dissolution under the effect of corrosive media (see Fig. 2, curve 5). Heat treatment of the films produced a marked increase in their corrosion resistance due to slower dissolution of the compacted structure (see Fig. 2, curve 6). The mechanism of interaction of the films where phase separation occurs and the corrosive medium is more complicated. The crystal phase is insoluble in both neutral

and acid media (see Fig. 2, curves 7 – 10), as a consequence of which instead of the films uniformly thinning under corrosion, the vitreous phase is selectively washed out and the film is transformed into a loose and porous coating.

It is of interest to note that the appearance of crystal phases in films most inclined to phase separation can be observed not only under heat treatment but sometimes also during their interaction with water immediately after their forming (see Fig. 2, curve 11).

It can be seen from the data obtained that the corrosion stability of the films and the solid glasses is minimum on introduction of V_2O_5 and maximum with CoO dopant. The difference in corrosion resistance at $pH = 7$ is much more significant (washing duration from several hours to days) than at $pH = 4$ (within the limits of 1 – 2 h).

It is known that the introduction of doping oxides in glass is used to modify the physicochemical properties of the glass in a desired direction. In the case of thin glass films formed on coated products that subsequently undergo technological operations related to the use of thermal treatment and corrosive media, it is expedient to avoid using dopants that destabilize the vitreous phase. Of the oxides considered in the present paper, these are the oxides of molybdenum and vanadium. Other investigated dopants to lead-borate glass do not stimulate phase separation in formation of thin films by the laser-deposition method, although some of them can cause crystallization in solid glasses. Cobalt oxide is an especially positive dopant in this respect. Possibly, CoO , in addition, has an inhibiting effect and impedes phase separation facilitated by other oxides.

Thus, the effect of high-energy plasma on thin vitreous films in the course of their formation by the laser-deposition method results in the formation of a more stable vitreous phase compared to low-energy methods. The increased stability of the vitreous phase suggests that in this case there are no reasons to assume complete absence of correlation between the properties of solid glasses and the properties of films based on them. Therefore, in predicting the crystallizing capacity and corrosion resistance of the three-component lead-borate-silicate thin glass films, in a first approximation one can rely on the properties of glasses of the same chemical composition that are in a volume state.

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